

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-68175

(43) 公開日 平成7年(1995)3月14日

(51) Int.Cl. ⁸	識別記号	庁内整理番号	F I	技術表示箇所
B 0 1 J 23/89	Z A B A	8017-4G		
B 0 1 D 53/86	Z A B			
53/94				
			B 0 1 D 53/ 36	Z A B
				1 0 4 A
			審査請求 未請求 請求項の数2	F D (全 5 頁)

(21) 出願番号 特願平5-168192

(22) 出願日 平成5年(1993)6月11日

(71) 出願人 000002967

ダイハツ工業株式会社

大阪府池田市ダイハツ町1番1号

(72) 発明者 田中 裕久

滋賀県蒲生郡竜王町大字山之上3000番地

ダイハツ工業株式会社滋賀テクニカルセン
ター内

(72) 発明者 高橋 一郎

滋賀県蒲生郡竜王町大字山之上3000番地

ダイハツ工業株式会社滋賀テクニカルセン
ター内

(74) 代理人 弁理士 野口 繁雄

(54) 【発明の名称】 排気ガス浄化用触媒

(57) 【要約】

【目的】 ペロブスカイト型複合酸化物を触媒成分とし、アルミナと共存させることによって高温でも高い比表面積を維持できるようにするとともに、 LaAlO_3 の生成を抑えて触媒作用を維持させるようにする。

【構成】 ペロブスカイト型構造の複合酸化物に、 ZrO_2 を添加したアルミナと、 Pd などの貴金属とを共存させる。さらに、 Ce 及び Zr を少なくとも含む耐熱性酸化物を共存させてもよい。

【特許請求の範囲】

【請求項1】 一般式 $Ln_{1-x}AxMO_3$ (Ln はCeを除く希土類金属、 A はCe又はアルカリ土類金属、 M は遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$) で示されるペロブスカイト型構造の複合酸化物と、 ZrO_2 を添加したアルミナと、貴金属とを少なくとも共存させた排気ガス浄化用触媒。

【請求項2】 Ce及びZr、又はさらにCe以外の希土類金属を含む、少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物をさらに共存させた請求項1に記載の排気ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は800℃より高温で用いても一酸化炭素(CO)、炭化水素(HC)及び酸化窒素(NO_x)の浄化能力に優れた排気ガス浄化用三元触媒に関するものである。

【0002】

【従来の技術】 希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物は、CO、HC及び NO_x を浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、特開昭60-82138号公報参照)。しかし、ペロブスカイト型複合酸化物触媒は800℃以下で使用するのを目的としており、自動車排ガス用触媒のように900℃以上の高温域において高い触媒活性を必要とし、かつ高温での耐久性も満足する必要がある場合には、十分な触媒とはいえない。すなわち、ペロブスカイト型複合酸化物は、900℃以上の高温で使用すると焼結して有効表面積が減少し、触媒活性が著しく低下する。

【0003】 また、ペロブスカイト型複合酸化物はCO、HCの浄化能力は優れているが、 NO_x の浄化能力がやや劣っており、自動車排ガス用の三元触媒として実用に供するには十分ではない。そこで、 NO_x 浄化能力を改善するために、ペロブスカイト型複合酸化物に貴金属を共存させればよいことが知られている。一方、アルミナ(酸化アルミニウム; Al_2O_3)は900℃以上の高温においても高い比表面積を維持することのできる優れたウォッシュコート材料として知られており、貴金属触媒では広く用いられている。そこで、ペロブスカイト型複合酸化物触媒を900℃以上というような高温で長時間用いることのできる三元触媒とするために、アルミナと共存させ、貴金属を添加することが考えられる。

【0004】

【発明が解決しようとする課題】 ペロブスカイト型複合酸化物をアルミナと共存させた場合、自動車排気ガス中や大気中で800℃程度の高温で使用していると、ペロブスカイト構造の組成中のLaがアルミナと反応して $LaAlO_3$ を生成することが判明した。この $LaAlO_3$

は触媒活性を持たず、これが生成することによって触媒作用の優れたペロブスカイト型結晶構造が破壊される問題が生じる。そこで、本発明はペロブスカイト型複合酸化物を触媒成分とし、アルミナと共存させることによって高温でも高い比表面積を維持できるようにするとともに、 $LaAlO_3$ の生成を抑えて触媒作用を維持させるようにした触媒を提供することを目的とするものである。

【0005】

【課題を解決するための手段】 本発明の触媒は、一般式 $Ln_{1-x}AxMO_3$ (Ln はCeを除く希土類金属、 A はCe又はアルカリ土類金属、 M は遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$) で示されるペロブスカイト型構造の複合酸化物と、 ZrO_2 を添加したアルミナと、貴金属とを少なくとも共存させた排気ガス浄化用触媒である。この触媒にはCe及びZr、又はさらにCe以外の希土類金属を含む、少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物をさらに共存させることができる。この耐熱性酸化物も800℃を越える高温において焼結を抑制し、高い比表面積を維持する作用をする。

【0006】 本発明の触媒は、例えば、 ZrO_2 を添加したアルミナと一般式 $Ln_{1-x}AxMO_3$ で示されるペロブスカイト型構造の複合酸化物とを少なくとも含む複合酸化物又は固溶体に、貴金属を担持させて製造することができる。その担持方法は、pHを4以下又は10より大きく調製した貴金属塩水溶液を用いて貴金属を含浸又は吸着させて担持させ、乾燥後に焼成する方法である。

【0007】 本発明では、アルミナとペロブスカイト型複合酸化物とを共存させて複合酸化物又は固溶体とする前に、アルミナに ZrO_2 を添加してアルミナ表面に ZrO_2 を分散させる点に特徴がある。アルミナ表面の ZrO_2 は800℃を越える高温においてアルミナの物質移動を抑制し、ペロブスカイト型複合酸化物中のLaとの反応による $LaAlO_3$ の生成を抑制する。これにより、触媒作用の優れたペロブスカイト型結晶構造は Al_2O_3 との共存下において、800℃を越える高温状態においても結晶構造が破壊されることなく、触媒活性を維持することができる。

【0008】 アルミナや耐熱性酸化物は一般に触媒成分の担体として用いられているのと同様の状態(形状、粒度、純度、比表面積)で用いればよい。例えば、比表面積は触媒成分を高分散状態に保持するため、 $20\text{m}^2/\text{g}$ 以上が望ましい。耐熱性酸化物中のCe、Zr、希土類金属の比率は特に制限されないが、Ceの100原子に対してZrは5~100原子、好ましくは5~50原子、Ce以外の希土類金属は0~100原子、好ましくは5~30原子の原子比となるように構成する。

【0009】 アルミナや耐熱性酸化物による効果は、触

媒成分をアルミナや耐熱性酸化物上に担持して用いる場合、及び触媒成分粉末とアルミナや耐熱性酸化物粉末とを混合して使用する場合のいずれの場合にも有効に発揮され、800℃を越える高温で長時間使用した後も触媒成分は担体上に高分散状態に維持されているか、又はアルミナや耐熱性酸化物粉末間に高分散の状態が存在している。

【0010】ペロブスカイト型複合酸化物それ自体も三元触媒として使用できるが、NO_xに対する浄化能力がHCやCOに対する浄化能力に比べてやや劣っている。そこで、NO_xに対する活性を高めるためにパラジウムなどの貴金属を少量添加した。貴金属はペロブスカイト型複合酸化物上及びアルミナ上に、又はさらに耐熱性酸化物上にも担持されている。担持された貴金属は反応するペロブスカイト型複合酸化物上では固溶及び析出現象が起こり、一方、反応しない高比表面積のアルミナや耐熱性酸化物上では析出状態で高分散に担持されることにより、排気ガス変動雰囲気下における800℃を越える高温でも貴金属の焼結が起きにくく、浄化活性が高度に維持される。

【0011】本発明における触媒成分の1つであるペロブスカイト型複合酸化物の割合は触媒全量の1～80重量%が望ましい。1重量%より少ない場合は触媒活性が低く、逆に80重量%より多くなるとアルミナや耐熱性酸化物の効果が現われにくくなり好ましくない。ペロブスカイト型複合酸化物の形状、粒度、純度、比表面積などは触媒成分として通常用いられる状態であればよい。

【0012】他の触媒成分である貴金属は白金族のRu、Rh、Pd、Os、Ir及びPtのうちから選ばれた1種又は2種以上を用いる。これらの貴金属のうちPdを用いた場合にNO_x浄化特性が最も向上する。貴金属の量は触媒全量に対し0.01～5重量%、望ましくは0.1～2重量%がよい。貴金属が0.01重量%より少ない場合はNO_x浄化能力の向上が不十分であり、逆に5重量%を越えてもNO_x浄化能力が飽和する。これら貴金属は従来の三元触媒において通常用いられている状態（形状、粒度、純度、比表面積）で用いる。このように、本発明にかかる触媒は、800℃を越える高温でも耐久性のある安価な排気ガス浄化用三元触媒となる。

【0013】本発明の触媒を製造する方法で貴金属を共存させる工程では、貴金属塩水溶液のpHを4以下とする製造方法の場合は、水溶性貴金属塩としてはPdCl₂、PtCl₂、RuCl₂・3H₂Oなどの塩化物、Pd(NO₃)₂、Ru(NO₃)₂、Rh(NO₃)₂などの硝酸塩、Pd(NO₃)₂(NH₃)₂、Pt(NO₃)₂(NH₃)₂などのジニトロジアミン塩など、水溶液が強酸性を示すものが好ましい。

【0014】貴金属塩水溶液のpHを10より大きくして製造する方法の場合は、テトラアミンパラジウムジク

ロライドPd(NH₃)₄Cl₂やテトラアミンパラジウム水塩Pd(NH₃)₄(OH)₂などの塩基性水溶液にアンモニア水や酸を添加してpH>10になるように調製して用いるか、PdCl₂、PtCl₂、RuCl₂・3H₂Oなどの塩化物、Pd(NO₃)₂、Ru(NO₃)₂、Rh(NO₃)₂などの硝酸塩、又はPd(NO₃)₂(NH₃)₂、Pt(NO₃)₂(NH₃)₂などのジニトロジアミン塩などの酸性水溶液にアンモニア水を添加してpH>10になるように調製して用いる。本発明の触媒は、これにバインダーを添加し、所定の形状に成形して用いたり、又は水を加えてスラリー状として基材に塗布して用いることもできる。

【0015】

【発明の効果】本発明ではペロブスカイト型構造の複合酸化物に、ZrO₂を添加したアルミナと、貴金属とを少なくとも共存させたので、800℃を越える高温でもペロブスカイト型結晶構造が破壊されることなく、活性を維持することができる。

【0016】

【実施例】

（実施例1）

手順A：アルミナの前処理

市販のγ-Al₂O₃粉末100重量部にイオン交換水50重量部を加え、攪拌して含浸させる。次に、硝酸ジルコニル（ZrO₂分40.12wt%）49.9重量部をイオン交換水50重量部に溶解し、先に含水させたγ-Al₂O₃粉末に加えて攪拌し、40℃で30分間保持して吸着させる。その後、110℃に昇温させたオーブン中で乾燥させる。30分ごとによく攪拌し、水分を飛散させた後、110℃で12時間乾燥させる。乾燥した粉末を、電気炉を用いて大気中で600℃で3時間焼成した後、乳鉢で180μm以下の大きさに粉砕し、微細なZrO₂を表面に分散させたAl₂O₃粉末を得た。Al₂O₃とZrO₂の重量比は10：2であった。

【0017】手順B：耐熱性酸化物の製造

アルミナとともに担体として用いることのある耐熱性酸化物は、市販の高比表面積の酸化セリウム粉末（CeO₂比表面積130m²/g、純度99.9%/TREO（全希土類酸化物））111.9gを用意し、これにオキシ硝酸ジルコニウム（ZrO(NO₃)₂）水溶液（液比重1.51、液中にZrO₂換算で25.0重量%含まれる）147.9g、及び硝酸イットリウム（Y(NO₃)₃）水溶液（液比重1.62、液中にY₂O₃換算で21.7重量%含まれる）26.0gを加え、よく攪拌して混合しながら110℃で10時間大気中で乾燥した。その後、大気中で600℃で3時間焼成を行ない、（Ce_{0.9}、Zr_{0.1}、Y_{0.01}）O₂複合酸化物を約150g得た。

【0018】手順C：ペロブスカイト型複合酸化物結晶粉末の製造方法

ペロブスカイト型複合酸化物（La_{0.9}Ce_{0.1}）（Fe_{0.9}

Co_{0.4})O₃粉末の調製方法を説明する。硝酸ランタン103.9g、硝酸セリウム26.1g、硝酸コバルト34.9g、硝酸鉄72.7gを純水に溶解した水溶液0.3リットルを用意した。次に、中和共沈剤として炭酸ナトリウム50gを溶解した水溶液0.5リットルを用意した。中和共沈剤を先の水溶液に滴下し、共沈物を得た。その共沈物を十分水洗し、濾過した後、真空乾燥した。これを600℃で3時間大気中で焼成後、粉碎し、その後、800℃で3時間大気中で焼成を行ない、さらに粉碎し、(La_{0.8}Ce_{0.2})(Fe_{0.6}Co_{0.4})O₃の粉末を作製した。

【0019】手順D：ペロブスカイト型複合酸化物の担持

手順Cで製造したペロブスカイト型複合酸化物粉末75重量部、手順Aで得たZrO₂処理済みのAl₂O₃粉末60重量部、手順Bで製造した耐熱セリア粉末15重量部、セリアソル（固形分10wt%）50重量部（固形分では5重量部）、及びジルコニアソル（固形分30wt%）3.3重量部（固形分では1重量部）を、全固形分が50wt%となるようにイオン水を58.7重量部

【0020】手順E：貴金属Pdの担持
硝酸パラジウム溶液（Pd濃度4.4wt%）をPd分で1.67重量部となるように38重量部計量し、イオン交換水50重量部を加え、pH<2（実測値はpH=1.8）に調製した。このパラジウム溶液に手順Dで得

*たハニカム状サンプルを浸漬し、40℃で2時間保持してPdを吸着させた。その後、120℃で12時間乾燥させた後、空气中で600℃で3時間焼成し、実施例1の触媒試料を得た。

【0021】（実施例2）実施例1における手順Dで、ペロブスカイト型複合酸化物粉末を7.5重量部とし、ZrO₂処理済みAl₂O₃粉末を40重量部とし、耐熱セリア粉末を35重量部とする他は、実施例1と同様の操作により実施例2の触媒試料を得た。

【0022】（実施例3）実施例1における手順Dで、ペロブスカイト型複合酸化物粉末を50重量部とし、ZrO₂処理済みAl₂O₃粉末を50重量部とし、耐熱セリア粉末を50重量部とし、手順EでのPd分を0.83重量部となるように18.9重量部の硝酸パラジウム溶液を計量する他は、実施例1と同様の操作により実施例3の触媒試料を得た。

【0023】（実施例4）実施例1における手順Dで、ZrO₂処理済みAl₂O₃粉末を75重量部とし、耐熱セリア粉末の添加を省いた他は、実施例1と同様の操作により実施例4の触媒試料を得た。

【0024】（比較例a）実施例1の手順Dにおいて、ZrO₂処理済みAl₂O₃粉末を未処理のAl₂O₃粉末に代えた他は実施例1と同様の操作により比較例aの触媒試料を得た。

【0025】（比較例b）すでに実用化されている自動車用触媒であるPt-Rh/Al₂O₃触媒を比較例bの触媒試料とした。Pt-Rh含有量は0.54重量部であった。実施例及び比較例の触媒仕様を表1に示し、それぞれの触媒活性の測定結果を表2に示す。表2は初期及び耐久試験後の50%浄化温度を示したものである。

【0026】

【表1】

	ペロブスカイト型複合酸化物	アルミナ	耐熱セリア	貴金属
実施例1	(La _{0.8} Ce _{0.2})(Fe _{0.6} Co _{0.4})O ₃ [75]	処理すみ[60]	(CeZrY)O ₂ [15]	Pd[1.67]
実施例2	(La _{0.8} Ce _{0.2})(Fe _{0.6} Co _{0.4})O ₃ [75]	処理すみ[40]	(CeZrY)O ₂ [35]	Pd[1.67]
実施例3	(La _{0.8} Ce _{0.2})(Fe _{0.6} Co _{0.4})O ₃ [50]	処理すみ[50]	(CeZrY)O ₂ [50]	Pd[0.83]
実施例4	(La _{0.8} Ce _{0.2})(Fe _{0.6} Co _{0.4})O ₃ [75]	処理すみ[75]	---	Pd[1.67]
比較例a	(La _{0.8} Ce _{0.2})(Fe _{0.6} Co _{0.4})O ₃ [75]	処理なし[60]	(CeZrY)O ₂ [15]	Pd[1.67]
比較例b	---	処理なし[100]	(CeZrY)O ₂ [50]	Pt-Rh [0.54]

〔 〕内の数値は重量部を表わす。

	初期50%浄化温度 (°C)			耐久後50%浄化温度 (°C)		
	CO	HC	NOx	CO	HC	NOx
実施例1	150	162	162	230	233	222
実施例2	161	180	168	231	242	220
実施例3	167	171	172	245	239	247
実施例4	171	178	180	262	246	253
比較例a	175	201	197	283	284	268
比較例b	192	207	197	285	298	281

【0028】触媒活性の測定と耐久試験は以下のように行なった。

触媒活性の測定

ハニカム状（セル数400/inch²）コーゼライト担体（直径30mm、長さ50mm）に担持されたそれぞれの試料を下記のモデルガスにて活性を測定した。ガス温度は触媒への入口ガス温度で示し、室温から昇温し、*

* NO、CO、HC（C₂H₄+C₂H₆）のそれぞれが初期濃度の50%に低下した温度を50%浄化温度とする。

【0029】また、リッチガスとリーンガスはそれぞれ1秒毎に切り換えた。触媒を通るガス流の空間速度（SV）は30,000/時間とした。

【0030】

	リッチガス	リーンガス
CO	2.6 %	0.7 %
HC (C ₂ 換算濃度)	0.19%	0.19%
H ₂	0.87%	0.23%
CO ₂	8 %	8 %
NO	0.17%	0.17%
O ₂	0.65%	1.8 %
H ₂ O	10 %	10 %
N ₂	残部	残部

【0031】耐久試験

上記のリッチガスとリーンガスを5秒毎に切り換えて900°Cで30分、750°Cで30分のサイクルを15回繰り返して耐久試験を行なった。耐久試験後にも前記の方法で触媒活性を測定した。本発明による触媒はいずれも比較例よりも50%浄化温度が低く、触媒活性に優れている。また、耐久試験後の触媒のX線回折による測定

の結果、比較例aでは触媒成分であるペロブスカイト型複合酸化物とアルミナが反応して生じたLaAlO₃（JCPDSカードNo. 31-0022）が検出されたが、各実施例の測定結果からはLaAlO₃は検出されなかった。この結果から、アルミナのZrO₂処理により、高温での劣化反応が抑制されていることが分かる。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-068175

(43)Date of publication of application : 14.03.1995

(51)Int.Cl.

B01J 23/89

B01D 53/86

B01D 53/94

(21)Application number : 05-166192

(71)Applicant : DAIHATSU MOTOR CO LTD

(22)Date of filing : 11.06.1993

(72)Inventor : TANAKA HIROHISA
TAKAHASHI ICHIRO

(54) CATALYST FOR PURIFICATION OF EXHAUST GAS

(57)Abstract:

PURPOSE: To inhibit the formation of LaAlO_3 and maintain catalytic action and maintain a large specific surface area even at high temp. by allowing a perovskite type multiple oxide as a catalytic component to coexist with alumina.

CONSTITUTION: A multiple oxide having a perovskite type structure is allowed to coexist with ZrO_2 added alumina and a noble metal such as Pd or to further coexist with a heat resistant oxide contg. at least Ce and Zr.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE

[Translation done.]

NOTICES

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The catalyst for exhaust gas purification which made the multiple oxide of the perovskite type structure shown by general formula $\text{Ln}_{1-x}\text{AxMO}_3$ (the rare earth metal except Ce and A are transition metals, and Ln is [Ce or alkaline earth metal, and M] all one sort or two sorts or more, and $0 < x < 1$), the alumina which added ZrO_2 , and noble metals live together at least.

[Claim 2] Ce and Zr, or the catalyst for exhaust gas purification according to claim 1 that made the heat-resistant oxide which contains rare earth metals other than Ce further, and with which at least the part serves as a multiple oxide or the solid solution live together further.

[Translation done.]

*NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Even if it uses this invention at an elevated temperature from 800 degrees C, it relates to the three way component catalyst for exhaust gas purification excellent in the purification capacity of a carbon monoxide (CO), a hydrocarbon (HC), and nitrogen oxide (NOx).

[0002]

[Description of the Prior Art] Utilization is expected as a cheap three way component catalyst for exhaust gas purification with which the multiple oxide which has the perovskite type structure which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, HC, and NOx (refer to JP,59-87046,A and JP,60-82138,A). However, the perovskite mold multiple oxide catalyst aims at using it below 800 degrees C, and when it is necessary to need high catalytic activity and it also needs to satisfy the endurance in an elevated temperature in a pyrosphere 900 degrees C or more like the catalyst for automobile exhaust, it cannot be said as sufficient catalyst. That is, it will sinter, if a perovskite mold multiple oxide is used at an elevated temperature 900 degrees C or more, and an effective-surface product decreases, and catalytic activity falls remarkably.

[0003] Moreover, although CO and the purification capacity of HC are excellent, the perovskite mold multiple oxide is a little inferior in the purification capacity of NOx, and they are not enough to present practical use as a three way component catalyst for automobile exhaust. Then, in order to improve NOx purification capacity, it is known that what is necessary is just to make noble metals live together in a perovskite mold multiple oxide. On the other hand, the alumina (aluminum oxide; aluminum 2O3) is known as an outstanding wash coat ingredient which can maintain a high specific surface area also in an elevated temperature 900 degrees C or more, and is widely used by the precious metal catalyst. Then, in order to consider as the three way component catalyst which can be used for a long time by high temperature which calls a perovskite mold multiple oxide catalyst 900 degrees C or more, it is made to coexist with an alumina and it is possible to add noble metals.

[0004]

[Problem(s) to be Solved by the Invention] When a perovskite mold multiple oxide was made to coexist with an alumina and it was used at the about 800-degree C elevated temperature in motor exhaust and atmospheric air, it became clear that La under presentation of a perovskite structure reacted with an alumina, and generated LaAlO3. This LaAlO3 does not have catalytic activity, but when this generates, the problem by which the perovskite mold crystal structure which was excellent in the catalysis is destroyed produces it. Then, this invention uses a perovskite mold multiple oxide as a catalyst component, and while enabling it to maintain a high specific surface area also at an elevated temperature by making it coexist with an alumina, it aims at offering the catalyst suppress [catalyst] generation of LaAlO3 and it was made to maintain a catalysis.

[0005]

[Means for Solving the Problem] The catalyst of this invention is a catalyst for exhaust gas purification which made the multiple oxide of the perovskite type structure shown by general formula $\text{Ln}_{1-x}\text{AxMO}_3$ (the rare earth metal except Ce and A are transition metals, and Ln is [Ce or alkaline earth metal, and M] all one sort or two sorts or more, and $0 < x < 1$), the alumina which added ZrO2, and noble metals live together at least. Ce and Zr, or the heat-resistant oxide that contains rare earth metals other than Ce further and with which at least the part serves as a multiple oxide or the solid solution can be made to live together further for this catalyst. This heat-resistant oxide also controls sintering in the elevated temperature exceeding 800 degrees C, and carries out the operation which maintains a high specific surface area.

[0006] The catalyst of this invention can make the multiple oxide or the solid solution which contains at least the multiple oxide of the perovskite type structure shown by the alumina and general formula $\text{Ln}_{1-x}\text{AxMO}_3$ which added ZrO2 able to support noble metals, and can be manufactured. The support approach is the approach of using the noble-metals salt water solution which prepared pH more greatly than 4 or less and 10, making noble metals sink in or adsorb, making support, and calcinating after desiccation.

[0007] In this invention, before making an alumina and a perovskite mold multiple oxide live together and considering as a multiple oxide or the solid solution, the description is in the point of adding ZrO2 to an alumina and making an alumina front face distributing ZrO2. ZrO2 on the front face of an alumina controls the mass transfer of an alumina in the elevated temperature exceeding 800 degrees C, and controls generation of LaAlO3 by the reaction with La in a perovskite mold multiple oxide. Thereby, the perovskite mold crystal structure which was excellent in the catalysis can maintain catalytic activity, without destroying the crystal structure also in the elevated-temperature condition which exceeds 800 degrees C under coexistence with aluminum 2O3.

[0008] What is necessary is just to use an alumina and a heat-resistant oxide in the condition (a configuration, grain size, purity, specific surface area) same with generally being used as support of a catalyst component. For example, more than 20m2/g of specific surface area is desirable in order to hold a catalyst component in the high distribution condition. Although especially the ratio of Ce in a heat-resistant oxide, Zr, and a rare earth metal is not restricted, Zr constitutes five to 50 atom, and rare earth metals other than Ce zero to 100 atom preferably five to 100 atom to 100 atoms of Ce so that it may become the atomic ratio of five to 30 atom.

[0009] When the effectiveness by the alumina or the heat-resistant oxide supports a catalyst component on an alumina or a heat-resistant oxide and it uses, And it is demonstrated effectively [in any / in the case of mixing and using catalyst component powder, and an alumina and heat-resistant oxide powder / case]. Also after carrying out long duration use at the elevated temperature exceeding 800 degrees C, the catalyst component is maintained by the high distribution condition on support, or exists in the condition of high distribution between an alumina or heat-resistant oxide powder.

[0010] Although it can be used as a three way component catalyst also in itself [perovskite mold multiple oxide], the purification capacity over NO_x is a little inferior compared with the purification capacity over HC or CO. Then, in order to raise the activity over NO_x, little addition of the noble metals, such as palladium, was carried out. noble metals — a PUROBUSU kite mold multiple oxide and alumina top — or it is further supported also on the heat-resistant oxide. When the supported noble metals are supported with a deposit condition by high distribution on the alumina of high specific surface area which does not react on the other hand, or a heat-resistant oxide by dissolution and a deposit phenomenon happening on the perovskite mold multiple oxide which reacts, also at the elevated temperature exceeding 800 degrees C under an exhaust gas fluctuation ambient atmosphere, sintering of noble metals cannot break out easily and purification activity is maintained by altitude.

[0011] 1 - 80% of the weight of the catalyst whole quantity of the rate of the perovskite mold multiple oxide which is one of the catalyst components in this invention is desirable. If catalytic activity is low and increases more than 80 % of the weight conversely when fewer than 1 % of the weight, the effectiveness of an alumina or a heat-resistant oxide is hard coming to appear and is not desirable. The configuration of a perovskite mold multiple oxide, grain size, purity, specific surface area, etc. should just be in the condition of usually being used as a catalyst component.

[0012] The noble metals which are other catalyst components use one sort chosen from among Ru, Rh, Pd, Os(es), Ir(s), and Pt(s) of a platinum group, or two sorts or more. When Pd is used among these noble metals, an NO_x purification property improves most. The amount of noble metals has 0.1 - 2 desirably good % of the weight 0.01 to 5% of the weight to the catalyst whole quantity. Even if improvement in NO_x purification capacity is inadequate when there are few noble metals than 0.01 % of the weight, and it exceeds 5 % of the weight conversely, NO_x purification capacity is saturated. These noble metals are used in the condition (a configuration, grain size, purity, specific surface area) of usually being used in the conventional three way component catalyst. Thus, the catalyst concerning this invention turns into a cheap three way component catalyst for exhaust gas purification which is durable also at the elevated temperature exceeding 800 degrees C.

[0013] At the process which makes noble metals live together by the approach of manufacturing the catalyst of this invention In the case of the manufacture approach which makes pH of a noble-metals salt water solution four or less As a water-soluble noble-metals salt, chlorides, such as PdCl₂, PtCl₂, and RuCl₃·3H₂O, Dinitro diamine salts of that a water solution indicates strong acid nature to be, such as nitrates, such as Pd (NO₃)₂, Ru (NO₃)₃, and Rh (NO₃)₃, Pd(NO₂)₂(NH₃)₂, and Pt(NO₂)₂(NH₃)₂, etc. are desirable.

[0014] In the case of the approach of making pH of a noble-metals salt water solution larger than 10, and manufacturing it Tetrapod amine palladium dichloride Pd(NH₃)₄Cl₂ and tetra-amine palladium oxalate (NH₃) (OH) Pd 4 [whether it prepares and uses so that aqueous ammonia and an acid may be added in basic water solutions, such as 2, and it may be set to pH>10 and] Nitrates, such as chlorides, such as PdCl₂, PtCl₂, and RuCl₃·3H₂O, and Pd (NO₃)₂, Ru (NO₃)₃, Rh (NO₃)₃, Or it prepares and uses so that aqueous ammonia may be added to aqueous acids, such as dinitro diamine salts, such as Pd(NO₂)₂(NH₃)₂ and Pt(NO₂)₂(NH₃)₂, and it may be set to pH>10. The catalyst of this invention adds a binder to this, it can fabricate and use for a predetermined configuration, or it can add water, can make it the shape of a slurry, and can also apply and use it for a base material.

[0015]

[Effect of the Invention] Activity can be maintained without destroying the perovskite mold crystal structure also at the elevated temperature exceeding 800 degrees C, since the alumina which added ZrO₂ to the multiple oxide of perovskite type structure, and noble metals were made to live together at least in this invention.

[0016]

[Example]

(Example 1)

Procedure A : The ion-exchange-water 50 weight section is added to the gamma-aluminum 2O₃ powder 100 weight section of pretreatment marketing of an alumina, and is agitated and infiltrated into it. Next, the zirconium nitrate (ZrO 2-minute wt(s)[40.12] %) 49.9 weight section is dissolved in the ion-exchange-water 50 weight section, and it holds for 30 minutes and is made to agitate in addition to 2Ogamma-aluminum 3 powder which carried out water previously, and to adsorb at 40 degrees C. Then, it is made to dry in the oven which carried out the temperature up to 110 degrees C. After agitating well every 30 minutes and dispersing moisture, it is made to dry at 110 degrees C for 12 hours. After calcinating the dry powder at 600 degrees C in atmospheric air for 3 hours using an electric furnace, the mortar ground in magnitude of 180 micrometers or less, and 2Oaluminum3 powder which made the front face distribute detailed ZrO₂ was obtained. The weight ratio of aluminum2O₃ and ZrO₂ was 10:2.

[0017] Procedure B : Heat-resistant oxide which has used as support with the manufacture alumina of a heat-resistant oxide, Commercial cerium oxide powder of high specific surface area (2/g CeO₂ specific surface area of 130m) 99.9% of purity and TREO(all rare earth oxides)111.9g are prepared. To this, 147.9g (contained 25.0% of the weight by ZrO₂ conversion in liquid density 1.51 and liquid) of oxy-zirconium-nitrate (ZrO₂ (NO₃)) water solutions, And 26.0g (contained 21.7% of the weight by 2OY₃ conversion in liquid density 1.62 and liquid) of nitric-acid yttrium (Y(NO₃)₃) water solutions was added, and it dried in 10-hour atmospheric air at 110 degrees C, having agitated well and mixing. Then, baking was performed at 600 degrees C in atmospheric air for 3 hours, and about 150g of O(Ce<SUB>0.65Zr 0.30Y0.05)2 multiple oxides was obtained.

[0018] Procedure C : The preparation approach of manufacture approach perovskite mold multiple oxide (La_{0.8}Ce_{0.2}) (Fe_{0.6}Co_{0.4}) O₃ powder of perovskite mold multiple oxide crystal powder is explained. 103.9g of lanthanum nitrates, 26.1g of cerium nitrates, 34.9g of cobalt nitrates, and 0.3l. of water solutions which dissolved 72.7g of iron nitrate in pure water were prepared. Next, 0.5l. of water solutions which dissolved 50g of sodium carbonates as a neutralization coprecipitater was prepared. The neutralization coprecipitater was dropped at the previous water solution, and the coprecipitate was obtained. The vacuum drying was carried out, after rinsing the

coprecipitate enough and filtering it. This was ground after baking in 3-hour atmospheric air at 600 degrees C, and it calcinated in 3-hour atmospheric air at 800 degrees C after that, and ground further, and the powder of $O(\text{Fe}(\text{La}_{0.8}\text{Ce}_{0.2})_{0.6}\text{Co}_{0.4})_3$ was produced.

[0019] Procedure D: The perovskite mold multiple oxide powder 75 weight section manufactured in the support procedure C of a perovskite mold multiple oxide, The aluminum₂O₃ powder 60 weight section [finishing / ZrO₂ processing] obtained in Procedure A, the heat-resistant Seria powder 15 weight section manufactured in Procedure B, They are 58.7 weight ***** and a ball mill about ion water so that total solids may become 50wt(s)% about the ceria sol (solid content 10wt%) 50 weight section (solid content 5 weight sections) and the zirconia sol (solid content 30wt%) 3.3 weight section (solid content 1 weight section). Mixing for 12 hours, it ground and the slurry was obtained. The excessive slurry was blown off and homogeneity was coated, after making this slurry flow into a cordierite honeycomb. The honeycomb behind a slurry coat was dried at 120 degrees C for 12 hours, it calcinated at 600 degrees C in air for 3 hours, and the honeycomb-like sample was obtained. The amount of support of the sample after baking was 180g per honeycomb capacity of 1l.

[0020] Procedure E: 38 weight sections measuring of the support palladium nitrate solution (Pd concentration 4.4wt%) of noble metals Pd was carried out so that it might become the 1.67 weight section by part for Pd, the ion-exchange-water 50 weight section was added, and it prepared to pH<2 (an actual measurement is pH=1.8). It was immersed, the honeycomb-like sample obtained in Procedure D in this palladium solution was held at 40 degrees C for 2 hours, and Pd was made to adsorb. Then, after making it dry at 120 degrees C for 12 hours, it calcinated at 600 degrees C in air for 3 hours, and the catalyst sample of an example 1 was obtained.

[0021] (Example 2) In the procedure D in an example 1, made perovskite mold multiple oxide powder into 75 weight sections, made 2Oprocessed [ZrO₂] aluminum₃ powder into 40 weight sections, and the heat-resistant Seria powder was made into 35 weight sections, and also the catalyst sample of an example 2 was obtained by the same actuation as an example 1.

[0022] (Example 3) Perovskite mold multiple oxide powder was made into 50 weight sections in the procedure D in an example 1, 2Oprocessed [ZrO₂] aluminum₃ powder was made into 50 weight sections, the heat-resistant Seria powder was made into 50 weight sections, and the palladium nitrate solution of the 18.9 weight sections was measured so that it might become the 0.83 weight section about a part for Pd in Procedure E, and also the catalyst sample of an example 3 was obtained by the same actuation as an example 1.

[0023] (Example 4) In the procedure D in an example 1, made 2Oprocessed [ZrO₂] aluminum₃ powder into 75 weight sections, and addition of the heat-resistant Seria powder was excluded, and also the catalyst sample of an example 4 was obtained by the same actuation as an example 1.

[0024] ((a) The example of a comparison) In the procedure D of an example 1, 2Oprocessed [ZrO₂] aluminum₃ powder was replaced with 2Oaluminum₃ unsettled powder, and also the catalyst sample of the example a of a comparison was obtained by the same actuation as an example 1.

[0025] ((b) The example of a comparison) 2OPt-Rh/aluminum₃ catalyst which is a catalyst for automobiles already put in practical use was made into the catalyst sample of the example b of a comparison. The Pt-Rh content was the 0.54 weight section. The catalyst specification of an example and the example of a comparison is shown in Table 1, and the measurement result of each catalytic activity is shown in Table 2. Table 2 shows 50% purification temperature after the first stage and a durability test.

[0026]

[Table 1]

	ペロブスカイト型複合酸化物	アルミナ	耐熱セリア	貴金属
実施例 1	$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Fe}_{0.6}\text{Co}_{0.4})\text{O}_3$ [75]	処理すみ [60]	$(\text{CeZrY})\text{O}_2$ [15]	Pd [1.67]
実施例 2	$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Fe}_{0.6}\text{Co}_{0.4})\text{O}_3$ [75]	処理すみ [40]	$(\text{CeZrY})\text{O}_2$ [35]	Pd [1.67]
実施例 3	$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Fe}_{0.6}\text{Co}_{0.4})\text{O}_3$ [50]	処理すみ [50]	$(\text{CeZrY})\text{O}_2$ [50]	Pd [0.83]
実施例 4	$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Fe}_{0.6}\text{Co}_{0.4})\text{O}_3$ [75]	処理すみ [75]	----	Pd [1.67]
比較例 a	$(\text{La}_{0.8}\text{Ce}_{0.2})(\text{Fe}_{0.6}\text{Co}_{0.4})\text{O}_3$ [75]	処理なし [60]	$(\text{CeZrY})\text{O}_2$ [15]	Pd [1.67]
比較例 b	----	処理なし [100]	$(\text{CeZrY})\text{O}_2$ [50]	Pt-Rh [0.54]

[]内の数値は重量部を表わす。

[0027]

[Table 2]

	初期 50%浄化温度 (°C)			耐久後 50%浄化温度 (°C)		
	CO	HC	NO _x	CO	HC	NO _x
実施例 1	150	162	162	230	233	222
実施例 2	161	180	168	231	242	220
実施例 3	167	171	172	245	239	247
実施例 4	171	178	180	262	246	253
比較例 a	175	201	197	283	284	268
比較例 b	192	207	197	285	298	281

[0028] Measurement and the durability test of catalytic activity were performed as follows.

Activity was measured for each sample supported by the measurement honeycomb-like (number of cells 400-/inch 2) cordierite support (the diameter of 30mm, die length of 50mm) of catalytic activity by the following model gas. The inlet gas temperature to a catalyst shows gas temperature, it carries out a temperature up from a room temperature, and makes purification temperature temperature to which each of NO, CO, and HC (C₃H₆+C₃H₈) fell to 50% of initial concentration 50%.

[0029] Moreover, rich gas and lean gas were switched for every second, respectively. Space velocity (SV) of the gas stream which passes along a catalyst was made into 30,000-/time amount.

[0030]

Rich gas Lean gas CO 2.6 % 0.7 % HC (C₁ conversion concentration) 0.19% 0.19% H₂ 0.87% 0.23% CO₂ 8 % 8 % NO 0.17% 0.17% O₂ 0.65% 1.8 % H₂O 10% 10 % N₂ Remainder Remainder [0031] The rich gas and lean gas of the durability test above were switched every 5 seconds, it repeated at 900 degrees C for 30 minutes, the cycle of 30 minutes was repeated 15 times at 750 degrees C, and the durability test was performed. Catalytic activity was measured by the aforementioned approach also after the durability test. 50%, each catalyst by this invention has low purification temperature, and excels the example of a comparison in catalytic activity. Moreover, although LaAlO₃ (JCPDS card No.31-0022) which the perovskite mold multiple oxide and alumina which are a catalyst component reacted, and was produced was detected in the example a of a comparison as a result of measurement by the X diffraction of the catalyst after a durability test, LaAlO₃ was not detected from the measurement result of each example. From this result, ZrO₂ processing of an alumina shows that the degradation reaction in an elevated temperature is controlled.

[Translation done.]